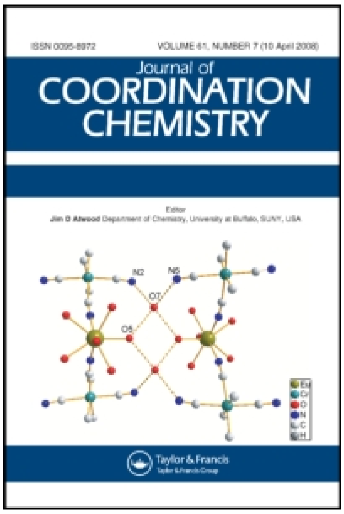

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HYPERSENSITIVITY IN COMPLEXES OF Nd(III) AND Ho(III) WITH MONOBASIC LIGANDS

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HYPERSENSITIVITY IN COMPLEXES OF Nd(III) AND Ho(III) WITH MONOBASIC LIGANDS

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Changes in the oscillator strengths of the hypersensitive f → f transitions of complexed Nd(III) and Ho(III) have been studied as a function of coordinating monobasic ligand in aqueous solution. For the transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ of Nd(III) and $^5I_8 \rightarrow {}^5G_6$, $^5F_1$ of Ho(III) a linear relation was found between the oscillator strength of the transition and the basicity of the ligand as measured by its acid constant. The utility of this correlation for gaining insight into some factors involved in the interaction of the ligand to the lanthanide cations and to protons is discussed.

INTRODUCTION

Although environmental hypersensitivity of certain lanthanide f → f transitions is a well documented observation,[1] the explanation for these intensity changes has remained a point of considerable discussion. Previous papers from this laboratory[2–4] have focussed on the possible roles which environmental symmetry, metal-ligand covalent bonding, and vibronically induced mechanisms could play in causing hypersensitivity.

The original proposal by Judd[5] that symmetry changes about the lanthanide ion could cause hypersensitivity can be paraphrased as follows. The necessary condition for intensity increases in the lanthanide f → f transitions is that odd parity electric field components be mixed into the excited state wavefunctions of the f orbital energy levels involved in the transition. Such mixing would, therefore, make the La Porte (parity) forbidden f → f transitions more allowed and their intensities should correspondingly increase. Symmetry changes in the lanthanide ion environment could accomplish this mixing if spherical harmonics of the type Y_{km} (with $k = 1$) were present in the crystal field around the metal ion. Symmetries belonging to the groups C_s, C_n ($n = 1,2,3,4,6$) or C_{nv} ($n = 2,3,4,6$) possess Y_{km} harmonics and, therefore, when hypersensitivity is observed, symmetries from the above mentioned groups must be present. However, several apparent exceptions to this symmetry requirement have been found.[6–9]

Judd[10] has also proposed that a vibronic mechanism could be a factor in the intensities of the f → f transitions. Although the intensity due to a vibronic mechanism was not explicitly considered in Judd's original paper, a number of authors have interpreted their results as either supporting[6,11] or discounting[1,12,13] this mechanism as a significant factor in hypersensitivity.

It has been suggested that a small amount of covalency is present in the lanthanide-ligand bonding.[2,3,6,14] Based on the experimental oscillator strengths of the hypersensitive bands of gaseous $NdBr_3$ and NdI_3, Gruen and DeKock[6] have indicated that hypersensitivity and covalency may be related. Subsequently, Henrie and Choppin[3] quantitatively related the oscillator strengths for hypersensitive transitions in several Nd(III) complexes with their corresponding nephelauxetic shifts. Based on the assumption that the nephelauxetic effect is a phenomenon of covalency, they suggested that the covalent bonding in the metal-ligand complex was directly related to hypersensitivity.

In this paper we consider the influence of complex formation in aqueous solution on the oscillator strengths of the Nd(III) and Ho(III) hypersensitive bands. Stability constants were used to calculate the concentrations of the various complex species in the aqueous solutions. Only ligands which formed inner sphere complexes were studied since previous work has shown that outer sphere complexation has little effect on the intensities of the lanthanide hypersensitive bands.[2,4]

EXPERIMENTAL

Materials

The neodymium and holmium perchlorate solutions were prepared by dissolving the oxides (American Potash and Chemical, 99.9%) in perchloric acid. These solutions were standardized by elution of aliquots through a column of Dowex-50 resin in the acid form. The eluted acid from the ion exchanger was titrated with standard base. The ligands used were (with purification procedure in parentheses): α-picolinic acid (recrystalized from benzene); acetylacetone (vacuum distilled at the lowest possible temperature and only the center fraction used); tropolone (recrystalized from ether and vacuum sublimed at 10^{-3} mm and 48°C); kojic acid (recrystalized from water and extracted several times with ether in a Soxhlet extractor using the lowest possible boiling temperature). Sodium fluoride, acetic acid and propionic acid were used without further purification. Stock solutions of these materials were prepared either gravimetrically or by standard acid-base titration procedures. Inert electrolyte ($NaClO_4$) was added to all solutions to provide the total ionic strength corresponding to the reference states for the stability constants.

Equipment

pH measurements were made with a Beckman Research Model 1019 pH meter and a Sargent Model S 30072-15 combination glass electrode. For measurements of solutions of high ionic strength, a 4.4 m NH_4Cl electrolyte solution was used in the glass electrode in place of the standard KCl electrolyte. This change provided a marked improvement in the stability of the electrode. The electrode was calibrated initially using a standard titration of HCl vs NaOH and the linear response between 0.01 and 0.001 m $[H^+]$ was extrapolated to higher concentrations of $[H^+]$. Subsequent standardizations were made with solutions of pH 4.01 buffer.

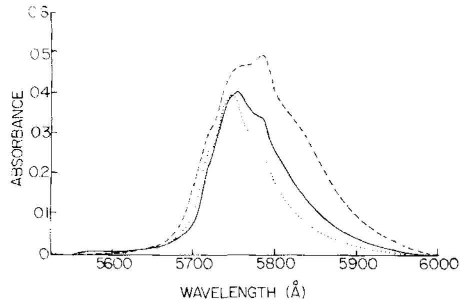


FIGURE 1 Absorption curves for the hypersensitive transition in Nd(III) $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$; $Nd^{+3}{}_{(aq)}$ · · ·, $NdAcac^{+2}$ – – – –, $NdOAc^{+2}$ ·–·–·–·–.

Spectral measurements were made at room temperature (ca. 23°C) using fused quartz cells of 2.0 or 5.0 cm. (nominal) path length. A Cary Model 14 recording spectrophotometer was suitably modified for obtaining digital spectra[15] and all spectra were run at a scanning speed of 2.5 Å/sec. and recorded digitally in 2.2 Å increments A CDC-6400 digital computer was used for all programmed calculations.

Procedure and Results

Nd(III) and Ho(III) were chosen as "typical" members of the light and heavy lanthanide series. Each has a hypersensitive transition relatively isolated from other interferences. The Nd(III) band designated as the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition (assuming Russell-Saunders coupling) situated between 5450 and 6100 Å, and the Ho(III) band lying between 4350 and 4637 Å, the $^5I_8 \rightarrow {}^5G_6, {}^5F_1$ transition were the hypersensitive bands used. All baselines returned to zero absorbance value except that of the 4637 Å side of the Ho(III) transition. In the worst case this baseline returned to 0.033 absorbance units but this was judged to not affect significantly the integrated band area used in the calculation of the oscillator strength.

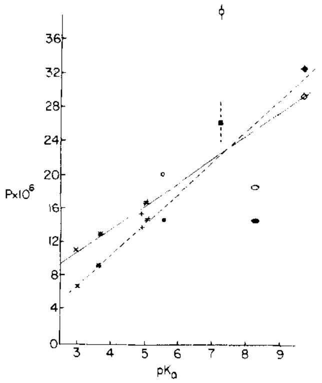


FIGURE 2 Plot of the oscillator strength, P, of 1:1 complexes vs the pK_a of the ligand acid; fluoride (X), glycolate (∗), acetate (+), propionate (≁), α-picolinate (○), tropolonate (▫), kojate (⬡), acetylacetonate (◇); Nd(III) ·–·–––, Ho(III) – – –.

The experimental oscillator strength, P_{exp}, was calculated from the equation

$$P_{exp} = 4.32 \times 10^{-9} \int \epsilon_i(\sigma)\, d\sigma \qquad (1)$$

where ϵ_i (σ) is the molar extinction coefficient at energy σ (cm^{-1}). In this work these values were calculated using the trapezoidal integration method.

The concentration of each metal-ligand complex in solution was calculated from the following material balance equations for total metal and total ligand concentrations (the conditions used prevented formation of any significant amounts of complexes greater than ML_3):

$$M_T = M + ML + ML_2 + ML_3 \tag{2}$$

$$L_T = ML + 2ML_2 + 3ML_3 + L + HL \tag{3}$$

where M and L refer to the metal and ligand respectively, the subscript T refers to the total concentrations, and the metal-ligand complex concentrations are expressed in terms of ML, ML_2 and ML_3. The uncomplexed protonated ligand concentration is referred to as HL. Based on the expression for the acid dissociation constant

$$K_a = \frac{[H]\,[L]}{[HL]} \tag{4}$$

and the metal-ligand complex stability constant expressions

$$\beta_i = \frac{[ML_i]}{[M]\,[L]^i} \tag{5}$$

equation (3) becomes, after some manipulation,

$$\begin{aligned} b\beta_3 L^4 &+ [b\beta_2 + K_a\beta_3(3M_T \quad L_T)]\; L^3 \\ &+ [b\beta_1 + K_a\beta_2(2M_T \quad L_T)]\; L^2 \\ &+ [b + K_a\beta_1(M_G \quad L_T)]\; L \quad K_a L_T = 0 \end{aligned} \tag{6}$$

where $b = K_a + H^+$.

In equation 6 all parameters are known except L. Using standard computational techniques the free ligand concentration was calculated and this, in turn, was used to obtain the concentrations of all the complex species from equations 2 and 5.

To prepare the solutions for spectroscopic measurement, two methods were used; either a ligand buffer solution was titrated into a metal ion solution or an acidic solution of metal and ligand was titrated with standard base. In both cases, after each titrant addition pH and spectral measurements were made. The tropolonate complexes required the second procedure involving titration by standard base since at pH values high enough for reasonable concentrations of complexed, unprotonated species, a deep yellow color developed which interfered with the spectra. With the base titration procedure the intensity of the yellow interference was considerably reduced; however, the possibility of formation of protonated metal complexes increases the uncertainty of the tropolonate data.

The oscillator strength for each metal complex (P_M, P_{ML}, etc) was calculated with equation (7) assuming the validity of Beer's Law.

$$P_{exp} = f_0 P_M + f_1 P_{ML} + f_2 P_{ML_2} + f_3 P_{ML_3} \tag{7}$$

The f_i values are the calculated mole fractions of the corresponding complexes. Computationally, the P parameters were fit using a linear regression program (BMD02R from the Health Sciences Facility at UCLA). A typical example of the experimental data and results of the f_i calculations are given in Table I for Ho(III) and α-picolinate. The complete data is found in reference 15. The oscillator strengths for individual complexes (calculated from equation 7) are given in Tables II and III for Nd(III) and Ho(III) respectively. The calculated P_M values which should be equal to the observed aqueous solution values for Nd(III) and Ho(III) (9.68 and 6.12 10^{-6} respectively) were allowed to be free parameters and served as a check on the validity of the data analysis. The results were least reliable for the tropolonate complexes which may be due to failure to take into account the proper amount of the protonated complex (see previous paragraph).

Representative spectra of $Nd^{+3}_{(aq)}$, $NdOAc^{+2}_{(aq)}$ and $NdAcac^{+2}_{(aq)}$ solutions are presented in Figure 1. The values of pK_a used in the calculations are included in Table II for each ligand.

DISCUSSION

The data in Tables II and III show that the oscillator strengths are different for different complexes. The

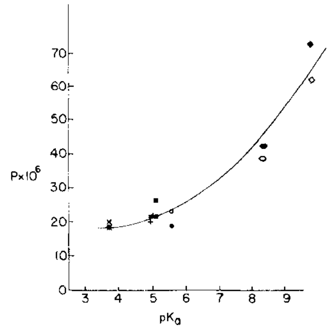


FIGURE 3 Plot of the oscillator strength, P, of 1:2 complexes of Nd(III) and Ho(III) vs the pK_a of the ligand acid; glycolate (NdX; Ho∗), acetate (Nd+, Ho≠), propionate (Nd□, Ho■), α-picolinate (Ndo, Ho●), kojate (Nd⬡, Ho⬢), acetylacetonate (Nd◇, Ho◆).

TABLE I
Data for the Ho(III) – α-Picolinate Solutions
I = 0.5 M, T = 23 ± 2°C

	pH	[M]	[ML]	[ML_2]	[ML_3]	[M_T]	[L]	[L_T]	P_{exp} ($x10^6$)
Conc (M)	2.801	.0110	0.0000	0.0000	0.0000	.01100	0.0000	0.00000	6.20
f_i		1.0000	0.0000	0.0000	0.0000	1.00000	0.0000	0.00000	
Conc (M)	2.386	.0082	.0026	.0002	.0000	.01100	.0000	.03018	8.000
f_i		.7462	.2337	.0197	.0003	1.00000	.0014	1.00000	
Conc (M)	2.526	.0075	.0031	.0004	.0000	.01100	.0001	.03018	8.549
f_i		.6820	.2851	.0321	.0007	1.00000	.0018	1.00000	
Conc (M)	2.671	.0067	.0037	.0006	.0000	.01100	.0001	.03018	9.139
f_i		.6071	.3401	.0513	.0015	1.00000	.0024	1.00000	
Conc (M)	2.807	.0059	.0043	.0008	.0000	.01100	.0001	.03018	9.723
f_i		.5320	.3886	.0764	.0030	1.00000	.0032	1.00000	
Conc (M)	2.947	.0050	.0047	.0012	.0001	.01100	.0001	.03018	10.415
f_i		.4525	.4312	.1106	.0057	1.00000	.0042	1.00000	
Conc (M)	3.080	.0042	.0051	.0017	.0001	.01100	.0002	.03018	11.096
f_i		.3788	.4606	.1508	.0098	1.00000	.0053	1.00000	
Conc (M)	3.231	.0033	.0053	.0022	.0002	.01100	.0002	.03018	11.932
f_i		.3010	.4776	.2040	.0174	1.00000	.0069	1.00000	
Conc (M)	3.372	.0026	.0052	.0028	.0003	.01100	.0003	.03018	12.606
f_i		.2363	.4768	.2589	.0280	1.00000	.0088	1.00000	
Conc (M)	3.517	.0020	.0051	.0035	.0005	.01100	.0003	.03018	13.389
f_i		.1799	.4600	.3166	.0435	1.00000	.0112	1.00000	
Conc (M)	3.742	.0012	.0045	.0044	.0009	.01100	.0005	.03018	14.600
f_i		.1131	.4098	.3994	.0777	1.00000	.0158	1.00000	
Conc (M)	3.890	.0009	.0040	.0049	.0012	.01100	.0006	.03018	15.232
f_i		.0814	.3666	.4445	.1075	1.00000	.0197	1.00000	
Conc (M)	4.052	.0006	.0035	.0053	.0016	.01100	.0007	.03018	15.946
f_i		.0561	.3168	.4812	.1459	1.00000	.0247	1.00000	
Conc (M)	4.263	.0004	.0028	.0056	.0022	.01100	.0010	.03018	16.715
f_i		.0343	.2546	.5085	.2026	1.00000	.0324	1.00000	
Conc (M)	4.448	.0002	.0023	.0057	.0028	.01100	.0012	.03018	17.432
f_i		.0225	.2075	.5150	.2550	1.00000	.0403	1.00000	
Conc (M)	4.631	.0002	.0019	.0056	.0034	.01100	.0015	.03018	17.856
f_i		.0151	.1690	.5095	.3064	1.00000	.0489	1.00000	
Conc (M)	4.772	.0001	.0016	.0055	.0038	.01100	.0017	.03018	18.238
f_i		.0113	.1451	.4999	.3436	1.00000	.0559	1.00000	
Conc (M)	5.016	.0001	.0013	.0053	.0044	.01100	.0020	.03018	18.643
f_i		.0074	.1145	.4787	.3995	1.00000	.0679	1.00000	

TABLE II

Oscillator strengths (x10^6) of Nd(III) complexes in aqueous solution for the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition.

	Fluoride	Glycolate	α-picolinate	Acetate (I=0.1M)	Acetate (I=2.0M)	Propionate (I=0.1M)
M^a	9.74±0.04	9.66±0.06	9.76±0.04	9.69±0.02	9.74±0.03	9.65±0.03
ML	10.00±0.27	11.53±0.10	17.90±0.12	13.71±0.12	13.28±0.19	14.95±0.38
ML_2		17.67±0.29	20.39±0.19	17.73±0.37	19.15±0.90	19.02±0.38
ML_3		17.35±0.99	25.91±0.62			
pK_a	2.94	3.57	5.20	4.55	4.80	4.78
	Propionate (I=2.0M)	Tropolonate	Kojate	Acetylacetonate		
M^a	9.59±0.03	8.71±0.32	9.75±0.07	9.36±0.06		
ML	13.74±0.20	34.47±0.82	16.45±0.26	25.91±0.26		
ML_2	19.40±0.88		33.99±0.54	54.22±1.94		
pK_a	4.95	6.69	7.61	8.88		

[a] The values for the oscillator strengths of $Nd^{+3}_{(aq)}$ listed for each ligand were determined from equation 7 and were not forced to be equal to the measured value of 9.68 x 10^{-6}

TABLE III

Oscillator strengths (x10^6) of Ho(III) complexes in aqueous solution $^5I_8 \rightarrow {}^5G_6, {}^5F_1$

	Fluoride	Glycolate	α-Picolinate	Acetate (I=0.1M)	Acetate (I=2.0M)	Propionate (I=0.1M)
M^a	6.10±0.06	6.02±0.10	6.18±0.04	6.05±0.03	6.03±0.03	6.08±0.02
ML	6.04±0.60	8.36±0.16	13.02±0.10	11.99±0.27	11.24±0.29	12.84±0.23
ML_2		16.48±0.44	16.93±0.16	18.21±0.80	21.09±1.06	23.22±0.91
	Propionate (I=2.0M)	Tropolonate	Kojate	Acetylacetonate		
M^a	6.15±0.04	4.66±1.05	6.17±0.10	5.65±0.20		
ML	12.44±0.37	23.00±2.08	12.84±0.28	28.73±0.34		
ML_2	24.84±1.18		37.31±0.49	63.48±0.97		

[a] The values for the oscillator strengths of $Ho_{(aq)}$ listed for each ligand were determined from equation 7 and were not forced to be equal to the measured value of 6.12 x 10^{-6}.

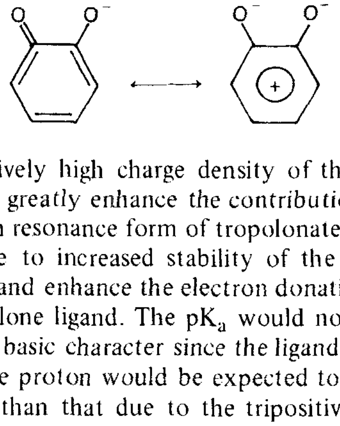
satisfactory agreement between the values of P_M calculated for the ligand solutions with that of the aqueous ion is strong evidence for the validity of the mathematical analysis. The data in Tables II and III further indicate that the oscillator strengths of the aqueous ion and of the complexes are not dependent on the ionic strength of the solution. Since it is likely that in the solutions of 2.0 M ionic strength, the high concentration of $NaClO_4$ results in extensive formation of outer sphere ion pairs between the aqueous lanthanide cation and perchlorate,[16] the independence of hypersensitivity to such ion pairing is again demonstrated.

For the 1:1 metal-ligand complexes of both neodymium and holmium, a linear correlation was found between the oscillator strength of the complex and the pK_a value of the ligand as shown in Figure 2. The correlation in Figure 2 is particularly striking when we consider that it is valid for a change of a factor of 4 in P_{ML} and 6 orders of magnitude in the acid constant of the ligand. Moreover, not only is the wide range of ligand basicity notable, but the variety in type of ligand is equally so since only kojate and tropolonate do not fall on the line. Fluoride, oxygen and nitrogen donor atoms can be involved in the complexes and both mono- and bidentate ligands are included. The extent of the correlation is strong evidence that the basicity of the ligand plays a major role in the intensity of the hypersensive transitions of the lanthanide ions.

Unfortunately, it is not possible to propose anything about the coordination number of the cation in these complexes or about the symmetry of the ML and ML_2 species. However, given the variety of ligand types, it would not seem likely that such a linear correlation could result from differences in the symmetry of the environment of the lanthanide cation. For the 1:2 complexes, we can see in Figure 3 that the correlation does not seem to be linear. The non-linearity may be a reflection of the greater uncertainty in P_{ML_2} due to the increased importance of β_2 (and β_3) in the calculation of $[ML_2]$, or it may reflect the increased importance of symmetry or coordination number changes in the 1:2 complexes.

A linear correlation between log β_1 and pK_a has been noted often in the past for a series of similar ligands with the same cation. However, a plot of P_{ML} vs log β_1 for our complexes did not correlate as well as that in Figure 2 which may be taken to indicate that the correlation in Figure 2 reflects something other than simply the strength of the total cation-ligand interaction (which is primarily ionic). We shall reserve further discussion of an interpretation of the correlation between the oscillator strength of the complex and the ligand basicity for a later paper.

Tropolonate and kojate are apparent exceptions to the correlation in Figure 2. Tropolonate would seem to require a larger value of pK_a to fit the curve, indicating that the ligand is more basic to the lanthanide ion than to a proton. Calvin[17] has proposed that the acidity of tropolonate is unusually high if the stability of its complexes with metal ions is used as a basis of comparison. He attributes this high acidity to the unfavorable distance between the oxygen atoms which results in weak hydrogen bonding. By contrast, in a chelate, the larger metal ion more easily bridges the oxygen-oxygen distance and the inherent strongly basic nature of tropolonate is exhibited. An alternate explanation for the enhanced stability of the metal-tropolonate is based on the behavior of the parent hydrocarbon, cycloheptatriene, which becomes an aromatic system when the cation (tropylium$^+$) is formed. In fact this is the most stable organic carbonium ion known.[18] In a similar fashion, the mono-ketone derivative, tropone, is greatly stabilized by contributions from a cycloheptatrienylium oxide or "zwitterion" resonance form.[19] It would not be unexpected, then, that the tropolone anion would likewise have resonance contributions from analogous structures.



The relatively high charge density of the lanthanide ion could greatly enhance the contributions from the zwitterion resonance form of tropolonate. This would contribute to increased stability of the coordinated complex and enhance the electron donating ability of the tropolone ligand. The pK_a would not reflect this increased basic character since the ligand polarization due to the proton would be expected to be considerably less than that due to the tripositive lanthanide ion. The failure of the tropolonate complex to fit the correlation may, then, reflect that the pK_a is not a true measure of the ligand basicity.

Based on the observed oscillator strengths, the kojate anion appears to be less basic than the pK_a values would indicate. Comparing the enthalpy and entropy of protonation for kojate, acetylacetonate and tropolonate anions, kojic acid appears to form very stable hydrogen bonds involving the keto and α-hydroxy oxygens.[20] Such internal hydrogen bonded structures are known to stabilize the protonated acid form and to increase the pK_a when compared to non-hydrogen bonded acids. In the case of kojate, then, the ligand basicity may be lower than indicated by the pK_a of the acid. Moreover, the kojate anion offers little possibility for a resonance stabilized system in the metal complex compared to the similar chelating ligands acetylacetone and tropolone. Finally, the kojate ligand has oxygen atoms which are not involved in complexation with the cation. It has been recently suggested that a water network between such hydrogen bonding sites and the inner coordination sphere could be especially stable.[21] Such a stable network might weaken the ligand-metal interaction and cause a decrease in the oscillator strength of the hypersensitive transitions of the cation.

The agreement of α-picolinate is interesting since only the pK_a value for the carboxylate group is used in Figure 2. Inasmuch as the correlation was much poorer for α-picolinate if the sum of the pK_a values for both the nitrogen and the carboxylate donors were used, this would seemingly imply that the lanthanide-nitrogen donor interaction is relatively weak. Sinha[22] has also noted that lanthanide-nitrogen donor interaction has little effect on the electronic spectra of lanthanide complexes in solution.

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